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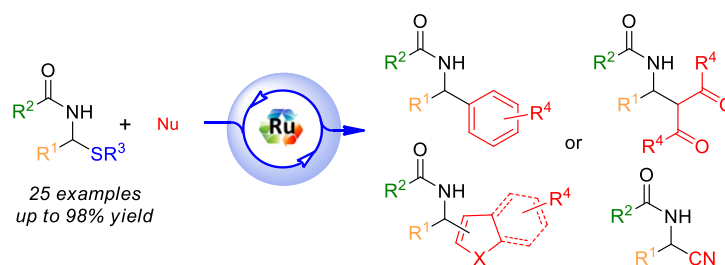
α -Carbamoylsulfides as *N*-Carbamoylimine Precursors in the Visible Light Photoredox-Catalyzed Synthesis of α,α -Disubstituted Amines

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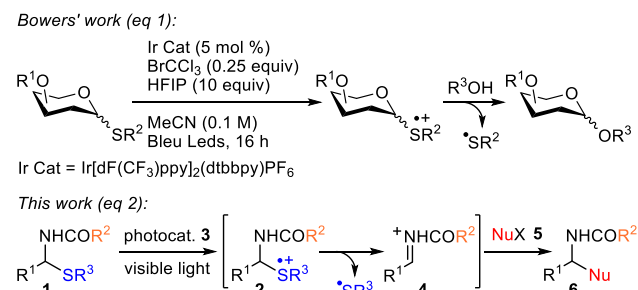
Supporting Information Placeholder



ABSTRACT: A general and practical photoredox-promoted addition of nucleophiles to *N*-acylimines generated *in situ* from α -amidosulfides using $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ as the photocatalyst is reported. The broad scope of the reaction toward various nucleophiles and amidosulfide derivatives was explored. This novel protocol provides a rapid, mild, and efficient access to valuable α,α -disubstituted amines in respectable yields.

The use of masked *N*-acyl and *N*-carbamoylimines has been proven to be a powerful strategy in the preparation of synthetically useful α -substituted amines.¹ Consequently, many precursors containing a good leaving group such as *O*-alkyl, OH, sulfone, halide, benzotriazole or amide have been investigated for the generation of imines (or iminium ions).² However, in some cases, strong acids or bases are required, which precludes the presence of acid- or base-sensitive functional groups. In this regard, we recently reported a NIS (*N*-Iodosuccinimide) mediated aza-Friedel-Crafts (aza-FC) reaction using α -carbamoylsulfide as easily available imine precursors.³ However, while the reaction proceeds under neutral and mild conditions, the formation of molecular iodine during the reaction can limit the substrate scope of the reaction.

Scheme 1. Proposed work hypothesis



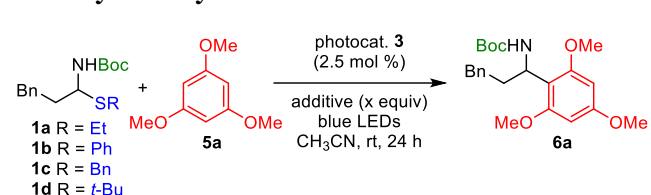
As a continuation of this research program, we sought to develop a new method for the preparation of *N*-carbamoylimines from α -carbamoylsulfides that would be mild, practical, and highly func-

tional-group-tolerant. Our approach was inspired by the work of Bowers,^{4,5} who showed that photo-oxidation of thioglycosides in the presence of Iridium photocatalyst, BrCCl_3 and visible light generates oxocarbenium ions, which can be then trapped with alcohols to form *O*-glycosides (Scheme 1, eq 1). We thought that visible light photocatalysis^{6,7} could be used to generate *in situ* the *N*-carbamoyliminium **2** from α -aminosulfides **1** under mild conditions (Scheme 1, eq 2). Indeed, the photoinduced single-electron oxidation of the neutral species **1** might produce a sulfur radical cation **2**. The latter could then undergo C-S bond cleavage to give an *N*-acyliminium ion **4**, which can proceed with nucleophiles to provide the addition product **6**.

To test this hypothesis, we selected an appropriate reaction for optimization. The initial studies focused on aza-FC reaction of *N*-acylimines generated *in situ* from α -amidosulfides. 1,3,5-Trimethoxybenzene (**5a**) was chosen as arene nucleophile with tert-butyl (1-(ethylthio)-3-phenylpropyl)carbamate (**1a**) as the substrate. To our delight, by using a Ruthenium photoredox catalyst **3a** in CH_3CN , we were able to isolate the desired aza-FC **6a** in 60 % yield (Table 1, entry 1). The yield was further improved by adding 10 equivalents of hexafluoroisopropanol (HFIP) or *t*-BuOH as a protic additive (entries 2 and 3). In particular, *t*-BuOH was chosen for the further optimization as it is cheaper. The amount of alcohol was also important, and less or more than 10 equivalents *t*-BuOH decreased the yield (entry 3 vs. entries 4 and 5). Although the role of alcohol is not fully understood, it may increase the solubility of radical cation **2** as described in previous reports.^{4,8} However, in the course of our electrochemical study, we found that the oxidation potential of **1a** was reduced in presence of *t*-BuOH (see Supporting Information) hence favoring the

formation of **4**. In contrast, no beneficial effect was observed when the reaction was performed in the presence of the hazardous BrCCl_3 as oxidative quencher (Table 1, entry 6).^{4,6} Different photocatalysts **3b-e** (entries 5-7) were also screened. While the organic photocatalyst Eosin Y **3e** (entry 9) was found to be a suitable catalyst for this reaction,⁹ better result was obtained with $[\text{Ru}(\text{bpy})_3(\text{PF}_6)_2]$ **3a** (entry 3). Next, we studied the reactivity in different solvents, and the yield significantly dropped when MeCN was replaced by tetrahydrofuran (THF), CH_2Cl_2 or *t*-BuOH (see Supporting Information). The reaction was improved further by increasing the substrate concentration (Table 1, entry 11). Further studies revealed that the nature of the substituent on the S atom of the α -amidosulfides influenced the efficiency of the reaction (entries 12-14). The use of S-aryl (**1b**, entry 12) and S-benzyl (**1c**, entry 13) derivatives resulted in lower yields than with the S-*t*-butyl (**1d**, entry 14) and S-Et (**1d**, entry 11) derivatives. It is noteworthy that no reaction occurred in the absence of a photocatalyst or light (Table 1, entries 15 and 16). These experiments indicate that the photoredox catalysis is essential for this process.

Table 1. Survey of reaction conditions for the photocatalyzed alkylation of 1.



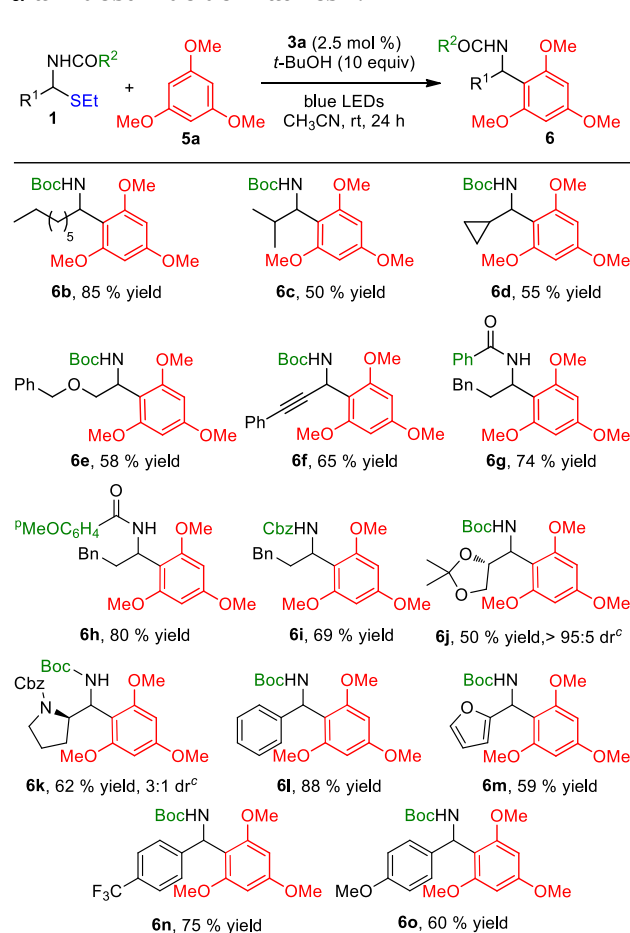
entry	1	photocat. 3	additive (x equiv)	6a yield (%) ^{a,b}
1	1a	$\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ (3a)	-	60
2	1a	3a	HFIP (10)	77
3	1a	3a	<i>t</i> -BuOH (10)	85
4	1a	3a	<i>t</i> -BuOH (5)	77
5	1a	3a	<i>t</i> -BuOH (20)	63
6	1a	3a	<i>t</i> -BuOH (10)	67 ^c
7	1a	$\text{Ru}(\text{bpy})_3\text{Cl}_2$ (3b)	<i>t</i> -BuOH (10)	65
8	1a	$\text{Ir}(\text{ppy})_2(\text{dtbbpy})(\text{PF}_6)$	<i>t</i> -BuOH (10)	70
9	1a	Eosin Y (3e)	<i>t</i> -BuOH (10)	63 ^d
10	1a	3a	<i>t</i> -BuOH (10)	60 ^e
11	1a	3a	<i>t</i> -BuOH (10)	90 ^f
12	1b	3a	<i>t</i> -BuOH (10)	57
13	1c	3a	<i>t</i> -BuOH (10)	63
14	1d	3a	<i>t</i> -BuOH (10)	91
15	1a	3a	<i>t</i> -BuOH (10)	- ^{h, i}
16	1a	3a	<i>t</i> -BuOH (10)	- ^h

^aGeneral conditions: **1** (0.10 mmol), 1,3,5-trimethoxybenzene **2a** (0.15 mmol), **3** (0.025 equiv), additive in MeCN (1.0 mL) irradiated at rt for 24 h. ^bYields referred to chromatographically pure product. ^c BrCCl_3 (0.025 mmol) was used as oxidative quencher. ^dIrradiated with green LEDs. ^eMeCN (2 mL) was used. ^fMeCN (0.5 mL) was used. ^hStarting material was recovered. ⁱWithout any irradiation.

We next examined the scope of α -amido or α -carbamoylsulfides **1** that participate in this photocatalyzed aza-FC reaction. As summarized in Scheme 2, the reaction of aliphatic α -carbamoylsulfides whether linear or α -branched, afforded the corresponding aza-FC adducts **6b-6e** in moderate to excellent yields. The photocatalytic system also proved to be efficient for various imines bearing functional groups such as benzyl ether (**1e**), acetal (**1j**) and amine (**1k**). Most remarkably, these imine precursors bearing an alkyne functional group such as (**1i**), which were totally unstable in our previous NIS-assisted protocol, worked well.^{3a} This was demonstrated as the α -carbamoylsulfides

1f being converted into the *N*-Boc propargylic amine **6f** which is an important building blocks for the synthesis of nitrogen-containing compounds.^{2m,10} Several protecting groups bonded to the nitrogen of **1**, including carbamates (**6a** and **6i**) and amides (**6g** and **6h**) were tolerated. We also found that, contrary to our previous studies,³ enantioenriched α -carbamoylsulfides **1j** and **1k** whose corresponding α -substituted imines are known to be sensitive towards racemization, were successfully engaged in this reaction.¹¹ For instance, the imine precursors derived from *D*-glyceraldehyde acetonide **1j** led to aza-FC adduct **6j** as a single diastereomer with no racemization. Similarly, *L*-proline derivative **1k** yielded to an enantiomerically pure mixture (3:1) of two inseparable diastereomers in 62 % yield. On the other hand, various aromatic and heteroaromatic α -amidosulfides effectively participated in this reaction, leading to the aza-FC adducts **6l-6m** in good yields. No noticeable difference in reactivity was observed when electron-rich and electron-poor functional groups were present in the aromatic ring (**6n** and **6o**).

Scheme 2. Substrate scope of the aza-FC reaction of α -amidosulfide derivatives 1.^{a,b}

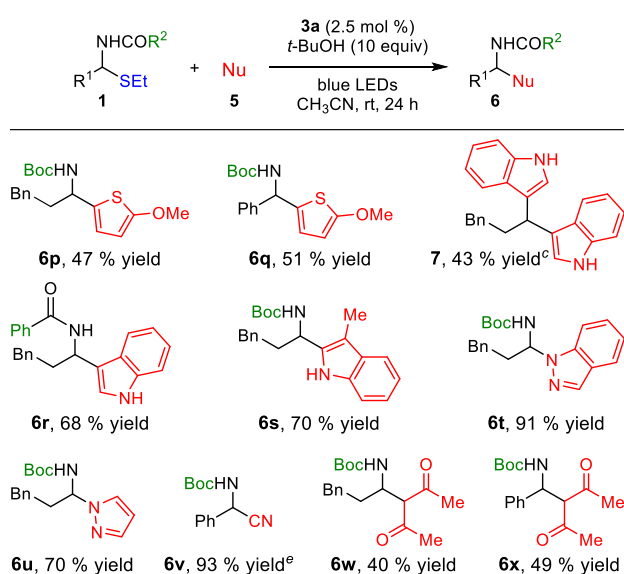


^aReaction conditions: **1** (0.10 mmol), 1,3,5-trimethoxybenzene **5a** (0.15 mmol), **3a** (0.025 equiv), *t*-BuOH (10.0 equiv) in MeCN (0.5 mL) irradiated at rt for 24 h. ^bYields referred to chromatographically pure product. ^cdr determined by ¹H-NMR analysis of crude mixtures

Extension of this novel photoredox protocol to other nucleophiles than **5a** was delightfully successful (Scheme 3). Under the same conditions, various heterocycles such as 2-methoxythiophene **5b** and indoles **5c-5d** afforded the C-alkylated aza-FC products **6p**, **6q**, **6r** and **6s** in moderate to good yields. It is worth noting that this is complementary to our early developed NIS-catalyzed approach in which the 3-alkylindoles furnished only *N*-alkylated

products.³ In the case of indole **5c**, bis(indolyl) product derived **7**, which display important biological activities,¹² was isolated as a single product. Interestingly, no acid was required to promote the double addition of **5c** to the *in situ*-generated *N*-Boc imine **1a**.^{2d-f,13} On the other hand, reaction of amide-protected **1g** with indole **5c** under similar reaction conditions only delivered the desired aza-FC product **6r**, indicating the influence of protecting groups on the reactivity of **4**. The process also worked with nitrogen nucleophiles such as indazole **5e** and pyrazole **5f** yielding to **6t** and **6u** in 91 % and 70 % yield, respectively. We further explored the potential for a Strecker-type reaction. Surprisingly, when attempting to trap the *N*-carbamoyl iminium **1a** with TMSCN, we did not isolate any desired product. Fortunately, the use of KCN **5g** was successful leading to **6v** in excellent yield. Next, we found that 1,3-dicarbonyls such as acetylacetone **5h** underwent addition to **1a** and **1l** yielding to Mannich product **6w** and **6x**. Although the yields were moderate, no acid or base was added to trigger the nucleophilic addition of **5h**.

Scheme 3. Substrate scope with respect to the nucleophile.^{a,b}

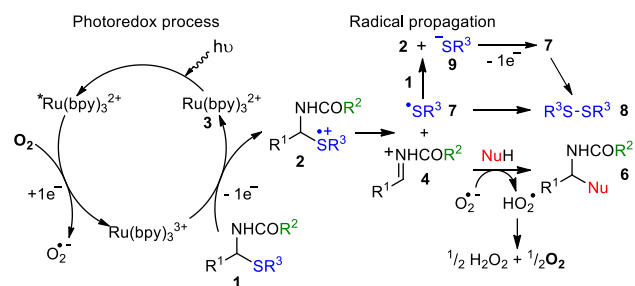


^aGeneral conditions: **1** (0.10 mmol), nucleophile **5** (0.15 mmol), **3a** (0.025 equiv), *t*-BuOH (10.0 equiv) in MeCN (0.5 mL) irradiated at rt for 24 h. ^bYields referred to chromatographically pure product. ^cFrom **1a**. ^dWith KCN (0.3 mmol) and a mixture MeCN:H₂O (0.5 mL:0.5 mL).

To gain more insight into the pathway of this photocatalytic reaction, several control experiments were conducted. We have first measured the oxidation potential of the α -carbamoylsulfides **1** used in our studies. The oxidation potential of the sulfur atom of **1a** was found to be 1.17 V vs. SCE in CH₃CN. This indicates that the electron-transfer pathway after its excitation of Ru²⁺ is not possible, as the oxidation potential of *Ru²⁺ (0.77 V vs. SCE in CH₃CN) is too low.^{6,14} To proceed, the reaction requires the formation of stronger oxidizing Ru³⁺ (1.33 V vs. SCE in CH₃CN) via oxidative quenching of *Ru²⁺. Since BrCCl₃ was an inefficient quencher (Table 1, entry 6), we hypothesized that molecular oxygen might act as an oxidative quencher of *Ru²⁺. Indeed, when the reaction was carried under anaerobic condition, only starting material **1a** was recovered (see Supporting Information), thus confirming the oxidative quenching role of molecular oxygen. A parallel experiment showed that the addition of oxygen results in slight decrease of reaction time (see Supporting Information). On the basis of the above results as well as other reports,^{6,15} a plausible mechanism for this process is outlined in Scheme 4. The oxidative quenching of *Ru²⁺ by the O₂ generates

the Ru³⁺ and superoxide radical anion (O₂^{•-}). Sulfur radical cation **2**, formed by the Ru³⁺-promoted oxidation of **1**, undergoes a fragmentation to generate the iminium **4**, S-centered radical (sulfanyl radical) **7** and Ru²⁺. Subsequent addition of nucleophiles to **4**, followed by hydrogen atom abstraction mediated by superoxide radical ion, provides the desired products **6** and hydroperoxyl radical (HO₂[•]). It is also possible that O₂ could be regenerated in course of disproportionation reactions of hydroperoxyl radical (HO₂[•]). This might explain why that addition of O₂ into the reaction medium was not necessary (see Supporting Information). Meanwhile the sulfanyl radical **7**, formed upon cleavage of the C–S bond, may evolve according to two different routes: a) either **7** dimerizes to form disulfide **8** or, b) **7** propagates the radical chain reaction by oxidation of **1** leading to **2** and thiolate anion **9**. The latter, based on the work Matsuda et al.,¹⁶ can be photooxidized to produce the disulfide **8** via **7**. To distinguish between these two plausible reaction pathways, we performed additional experiments. We irradiated **1a** in presence of 1,3,5-trimethoxybenzene (**5a**) and **3a** with blue LEDs for 1 h (see Supporting Information). In this condition, **6a** was isolated in 8 % yield (instead of 90 % after 24 h of irradiation, Table 1, entry 11). However, an increase in yield (30 %) was obtained when **1a** was stirred under dark conditions for 24 h after 1 h irradiation. These latter experiments indicate that although chain-propagating one-electron oxidation by **7** seems effective, it is not the dominant pathway. Consequently, it is reasonable to assume that **2** was mainly generated by electron transfer from the oxidized Ru³⁺ photocatalyst.

Scheme 4. Plausible reaction mechanism.



In summary, we have developed a practical photoredox-catalyzed synthesis of *N*-carbamoyl α,α -disubstituted amines from readily available α -amidosulfides under mild conditions. This methodology has wide scope, including several examples of nucleophiles, and moderate to excellent yields. A promising asymmetric amine synthesis with excellent diastereoselectivity was also achieved by using a chiral α -amidosulfides. Moreover, the photoredox protocol relies on the use of nonhazardous chemicals, features a simple experimental procedure, and is performed under mild conditions. We believe that such a protocol could find useful applications in view of the synthesis of functionalized building blocks, potentially biologically active substances, and natural products.

ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures and spectral data for all new compounds are provided. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

*These authors contributed equally. All authors have given approval to the final version of the manuscript.

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